

FINAL REPORT
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***Studies of Trace Gas Chemical Cycles Using Observations,
Inverse Methods and Global Chemical Transport Models***

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RESEARCH ACCOMPLISHMENTS: 1998 – 2001

We briefly summarize here research accomplishments over the period 1998 to the present supported in whole or in part by NASA Grants NAG-1-1805 and NAG-1-2152. Most of the work has been published in a large number of papers in journals and three theses (abstracts of papers and theses are attached as Appendix 1). The research accomplishments are divided conveniently into five sections devoted respectively to three-dimensional modeling; trace gas source and sink determinations; lifetime determinations; parametric uncertainty analysis; and ozone assessments.

1 Three-dimensional modeling

For interpreting observational data, and in particular for use in inverse methods, accurate and realistic chemical transport models are essential. Toward this end we have, in recent years helped develop and utilize a number of three-dimensional models including the Model for Atmospheric Transport and Chemistry (MATCH; Mahowald et. al., 1997a,b; Rasch et. al., 1997; Lawrence et. al., 1999). Under this current grant, we have utilized MATCH in a study of methyl bromide:

Jensen, C.D., Terrestrial Sources and Sinks of Atmospheric Methyl Bromide: Three-dimensional modeling of tropospheric abundance and sensitivities, S.M. Thesis, MIT-CGCS Report No. 62, 41 pgs., 1999.

We have also developed coupled models of convection and clouds including the following papers supported in part by this grant:

Wang, C. and R.G. Prinn, On the roles of deep convective clouds in tropospheric chemistry, *J. Geophys. Res.*, 105, 22269-22297, 2000.

Wang, C. and R.G. Prinn, Interactive chemistry and climate models in global change studies, *Recent Developments in Geophysics*, 2, 113-123, 1999.

Wang, C. and R.G. Prinn, Impact of the horizontal wind profile on the convective transport of chemical species, *J. Geophys. Res.*, 103, 22063-22071, 1998.

We have also developed a very detailed chemical process model for the remote marine atmosphere including the full oxidation scheme for dimethyl sulfide and used it to interpret ACE-1 data. This model is now being incorporated into MATCH.

Lucas, D.D. and R.G. Prinn, Mechanistic Studies of dimethyl sulfide oxidation products using an observationally constrained model, *J. Geophys. Res.*, submitted, 2001.

2 Time-variable regional source-sink determinations using inverse methods in 3D models

One of the major problems in atmospheric chemistry today involves the quantitative determination of trace gas emission and removal rates on regional as well as global scales. For example, the chemical and climatic importance of atmospheric CH_4 is readily recognized and ample evidence exists demonstrating an increase (albeit decelerating) in total global methane in recent years. However, estimates of the strengths of the individual regional surface sources of CH_4 which contribute to this global total are very uncertain.

Two new methods for estimating time varying fluxes of atmospheric trace gases using observations and 3D transport models have been investigated. One method used Kalman filtering to estimate inputs from a state-space model identified using unit-pulse response functions from the transport model. The method is new because no assumptions about initial conditions are required but deduced flux processes (e.g., chemical loss rates) must be linearly related to concentrations. Applied to AGAGE CCl_3F observations, the method is stable but estimated regional emissions were of poor accuracy due apparently to the inaccuracies in the ANU Lagrangian chemical transport model used in the analysis. This work by then MIT postdoctoral scientist J. Mulquiney was published in:

Mulquiney, J.E., and J.P. Norton, A new inverse method for trace gas flux estimation 1. State-space model identification and constraints, *J. Geophys. Res.*, 103, 1417-1427, 1998.

Mulquiney, J.E., J.A. Taylor, A.J. Jakeman, J.P. Norton and R.G. Prinn, A new inverse method for trace gas flux estimation 2. Application to tropospheric CFCl_3 fluxes, *J. Geophys. Res.*, 103, 1429-1442, 1998.

We have also completed a detailed review of inverse methods for trace chemicals including a novel section devoted to methods of incorporating model error into trace gas inversion studies.

Prinn, R.G., Measurement equation for trace chemicals in fluids and solution of its inverse, in *Inverse Methods in Global Biogeochemical Cycles*, ed. P. Kasibhatla *et al.*, *Geophysical Monographs*, No. 114, American Geophysical Union, pgs. 3-18, 2000.

Finally, we have recently completed estimation of regional emissions (1 degree by 1 degree grid) of three shorter-lived chlorocarbons using the NOAA-ARL Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT-4) model together with high frequency measurements. The work demonstrates the usefulness of this approach to check industry-based emission estimates.

Kleiman, G. and R.G. Prinn, Measurement and deduction of emissions of trichloroethene, tetrachloroethene and trichloromethane (chloroform) in the Northeastern U.S. and Southeastern Canada, *J. Geophys. Res.*, 105, 28875-28893, 2000.

Kleiman, G., Measurement and deduction of emissions of short lived atmospheric organochlorine compounds, Ph.D. Thesis, *MIT-CGCS Report No. 64*, 68 pgs., 1999.

3 Lifetimes and emissions of present and alternative halocarbons

Analysis of the extensive ALE/GAGE/AGAGE(AGA) observations (1978-present) of trace gases using our inverse methods with a 2D model was supported in part by this grant as well as by the separate AGA grant to MIT. This work has appeared in a series of papers from 1998 through 2001:

- Prinn, R.G., J. Huang, R.F. Weiss, D.M. Cunnold, P.J. Fraser, P.G. Simmonds, C. Harth, P. Salameh, S. O'Doherty, R.H.J. Wang, L. Porter, B.R. Miller, and A. McCulloch, Evidence for significant variations of atmospheric hydroxyl radicals in the last two decades, *Science*, 292, 1882-1888, 2001
- O'Doherty, S., D. Cunnold, G.A. Sturrock, D. Ryall, R.G. Derwent, R.H.J. Wang, P. Simmonds, P.J. Fraser, R.F. Weiss, P. Salameh, B.R. Miller and R.G. Prinn, In-Situ Chloroform Measurements at AGAGE Atmospheric Research Stations from 1994-1998, *J. Geophys. Res.*, in press, 2001.
- Prinn, R.G. and J. Huang, Comment on "Global OH trend inferred from methylchloroform measurements" by M. Krol *et al.*, *J. Geophys. Res.*, in press, 2001.
- Prinn, R.G., R.F. Weiss, P.J. Fraser, P.G. Simmonds, D.M. Cunnold, F.N. Alyea, S. O'Doherty, P. Salameh, B.R. Miller, J. Huang, R.H.J. Wang, D.E. Hartley, C. Harth, L.P. Steele, G. Sturrock, P.M. Midgley, and A. McCulloch, A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *J. Geophys. Res.*, 115, 17751-17792, 2000.
- Simmonds, P.G., S. O'Doherty, J. Huang, R.G. Prinn, R.G. Derwent, D. Ryall, G. Nickless, and D.M. Cunnold, Calculated trends and the atmospheric abundance of 1,1,1,2-tetrafluoroethane, 1,1-dichloro-1-fluoroethane, and 1-chloro-1,1-difluoroethane using automated *in-situ* gas chromatography mass spectrometry measurements recorded at Mace Head, Ireland, from October 1994 to March 1997, *J. Geophys. Res.*, 103, 16029-16037, 1998.
- Simmonds, P.G., D.M. Cunnold, R.F. Weiss, R.G. Prinn, P.J. Fraser, A. McCulloch, F.N. Alyea, and S. O'Doherty, Global trends and emission estimates of CCl₄ from *in-situ* background observations from July 1978 to June 1996, *J. Geophys. Res.*, 103, 16017-16027, 1998.
- Miller, B.R., J. Huang, R.F. Weiss, R.G. Prinn, and P.J. Fraser, Atmospheric trend and lifetime of chlorodifluoromethane (HCFC-22) and the global tropospheric OH concentration, *J. Geophys. Res.*, 103, 13237-13248, 1998

There is also one MIT doctoral thesis in this area advised by the PI:

Huang, J., Optimal determination of Global tropospheric OH concentrations using multiple trace gases, Ph.D. Thesis, MIT-CGCS Report No. 65, 163 pgs., 2000.

4 Parametric uncertainty analysis

Uncertainty analysis for complex models has been hampered in the past by the computational demands of these models. This has prevented the large number of runs (e.g., 10^3 - 10^4) required, for example, for the usual Monte Carlo approaches for models with many uncertain inputs or internal parameters. With support from the predecessor of this grant, we developed at MIT a new method for deducing the probability distribution functions (PDFs) of model outputs given the PDFs of uncertain inputs/parameters. The method uses expressions for model outputs which are chaos expansions of polynomials, whose recursive generating process incorporates weighting functions which are the PDFs of the inputs, together with a formalism for identifying the specific input values (collocation points) for running the parent complex model to deduce the coefficients of the expansion. The new theory (Probabilistic Collocation Method, Tatang et. al., 1997; Pan et. al., 1997) was used in the following 1998 paper:

Pan, W., M.A. Tatang, G.J. McRae, and R.G. Prinn, Uncertainty analysis of *indirect* radiative forcing by anthropogenic sulfate aerosols, *J. Geophys. Res.*, 103, 3815-3823, 1998.

5 1998 Ozone Assessment

The PI was a lead author on the first chapter of the WMO/NASA/NOAA/UNEP/EC-sponsored 1998 assessment of current knowledge of the ozone layer published in 1999:

Prinn, R.G., and R. Zander, with 30 other authors, Long-lived ozone-related compounds, in *Scientific Assessment of Ozone Depletion: 1998*, UNEP/WMO, Geneva, Chapter 1, pgs 1.1-1.54, 1999.